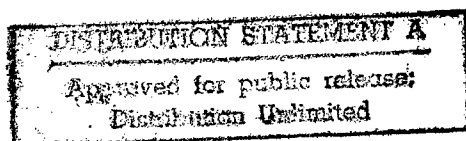# POLYMER ELECTROLYTE THROUGH ENZYME CATALYSIS FOR HIGH PERFORMANCE LITHIUM-ION BATTERIES

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This project was initiated with the idea of using enzyme catalysis as an efficient means for the synthesis of high conductivity polymer electrolytes by grafting amorphous segments of an ionically conductive polymer onto a monomer which can be easily polymerized *via* enzyme catalysis. The goal was to lock the ionomer segments onto a polymer backbone such that chemical and electrochemical stability is achieved. We have successfully polymerized such systems in aqueous media and characterized them.

Characterization of the polymers synthesized in this effort yielded very encouraging results as far as ionic conductivity goes, approaching an unprecedented room-temperature value of 10^{-3} S/cm. The various characterization efforts have indicated that thermal properties of the resulting compounds are such that these materials are excellent candidates for lithium-ion battery development. Furthermore, the processes used to achieve the final product yield very good mechanical properties. Battery testing using such electrolytes has shown that the solvent-free electrolyte provides good wettability of the electrodes. Because of the high lithium ion mobility, charge/discharge characteristics at and below room temperature proved that our novel polymer electrolyte has the potential, once optimized, to yield high performance batteries.

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Polymer Electrolyte through Enzyme Catalysis for High Performance Lithium-Ion Batteries

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Executive Summary

This project was initiated with the idea of using alternative means for the synthesis of polymer electrolytes with high yield, efficiency and ease of the processes used. Enzyme catalysis meets these criteria, and was used for this purpose by incorporating amorphous segments of poly (ethylene glycol), PEG, onto a monomer which can be easily polymerized *via* enzyme catalysis. The goal was to lock the PEG segments onto a polymer backbone such that chemical and electrochemical stability is achieved. To accomplish this task, we have substituted the basic monomer with PEG segments of various molecular weights. We have successfully polymerized such systems in aqueous media and characterized them.

Characterization of the polymers synthesized in this effort yielded very encouraging results as far as ionic conductivity goes, approaching an unprecedented room-temperature value of 10^{-3} S/cm. The various characterization efforts have indicated that although the glass transition temperature (T_g) is low, the melt and decomposition temperatures are high enough for use of such materials in lithium ion batteries in a wide temperature range. The low T_g is due to the high mobility of the PEG component, and the good thermal stability is due to the carrier polymer obtained *via* enzyme catalysis.

However, we went beyond this point and prepared a proprietary formulation, which takes advantage of the collective properties of the different components, and where the PEG segments become much longer through this process, without compromising their much-needed amorphous character. A fully solid-state system with high fluidity of the PEG segments has resulted.

We have also experimented with novel ionic gels based on our polymers without the incorporation of solvents as is usually the case in other efforts which employ propylene carbonate and the likes. Such materials are highly porous, with a strong ionic character, and would be developed further in the Phase II program.

The most direct way to test any material whether it is a good electrolyte or not is to sandwich it between two electrodes, an anode and a cathode, and evaluate the resulting battery. This is what we have done by using lithium anode and two high-energy cathode materials. In addition to using the appropriate electrodes, we have chosen to work with a novel current collector, polymer-based and thus thin and flexible. Another important advantage of the latter is that corrosion, experienced with metal current collectors, in the long run is avoided. Battery characterization and cycling results between 0°C and room temperature indicate that our electrolyte has the potential to yield high-energy capacity lithium ion batteries, which will be marketed in collaboration with our partner who has been producing energy storage devices for a good number of years.

Purpose of the Research

Polymer electrolytes are of prime interest in the development of advanced battery systems. Unfortunately, persistent problems associated with these materials when used with high-energy anodes such as lithium have accelerated the pace of this development. Despite setbacks, the quest for a truly solid-state lithium battery continues because of the unique design capabilities offered by this type of architecture and the potential for improved safety in high rate systems.

High conductivity and wide electrochemical stability, as well as compatibility with electrode materials are three criteria in choosing a suitable electrolyte for practical battery applications. One of the main problems encountered with polymer electrolytes is the short cycle life of cells containing these materials. Impedance and polarization studies have implicated passivation of the lithium anode as the reason for the observed degradation of cell behavior. The passivating film is known to result from reaction between the polymer electrolyte and lithium. This reaction is fostered by the requirement to operate conventional (although experimental) solid state lithium batteries at temperatures in excess of 100° C. This operating condition is due to the high glass transition temperature (T_g) of the polymer hosts presently used for polymer electrolytes. These materials include poly(ethylene oxide), PEO, which is a polycrystalline solid material at room temperature. As a result of this characteristic, polymer electrolytes incorporating such materials exhibit low conductivities (in excess of 10^{-7} S/cm) at room temperature.

Room temperature operation of lithium ion batteries, which use polymer electrolytes having the appropriate thermal, electrical and mechanical characteristics could solve many of the technical problems currently faced by this technology. Conventional approaches to the development of new solid polymer electrolytes have relied heavily on evolutionary changes in the basic recipe of the polymer/salt complex. Introducing solvents such as propylene carbonate or ethylene carbonate has contributed to the ionic conductivity and the better mobility in general of the lithium ion. The increased conductivity is without a doubt a favorable characteristic when compared with their parent solid electrolytes. However, the so-called gel systems are thermodynamically unstable. Gelled electrolytes may undergo solvent exudation upon long storage, especially under open-atmosphere conditions. This phenomenon is known as the "Syneresis" effect {1,2}. Furthermore, the solvents tend to decompose at the high voltages characteristic of lithium-ion batteries and react with the electrodes and the polymer host.

Our Phase I research sought to demonstrate that novel polymer electrolytes can be synthesized by alternative means to what is conventionally known, so that low-T_g PEO segments bound to solid matrix with improved ionic conductivity can operate in a wide range of temperatures. Lowering the operating temperature of solid-state lithium cells would provide a major contribution toward lengthening cycle life and improving stability.

The Phase I approach took a new direction in this area of research. Our direction consisted of the design of defined fluid ionic pathways, yet fixed onto a solid-state carrier, thus facilitating cation transport across the polymer electrolyte layer. This is not the case with electrolytes such as PEO where the amorphous regions of the polymer are not directly connected and the amorphous character of the polymer is related to its temperature. We, in turn, have synthesized and characterized a family of novel polymer electrolytes prepared by using the enzyme catalysis technique used by the US Army Soldiers Command team (Natick, MA) {3} of monomers designed for such an application.

The basic concept, which will be given in the approach section, for our research consisted of derivatising phenol with a PEO segment (in this case PEG) whose length is high enough to efficiently transport lithium ions, and the subsequent polymerization of the phenol derivative through enzyme catalysis. In this type of architecture, the phenol segments provide for thermal and mechanical stability of the system while maintaining the fluidity of the fixed PEG units to accommodate lithium ion transport efficiently.

As an extension to this concept, the resulting phenol/PEG polymer is locked in a totally solid-state 3-D system *via* the sol gel processing technique. The latter technique appears to improve the chemical stability of the PEG segments when in contact with lithium. The unique structure of our material has resulted in unprecedented conductivities approaching 10^{-3} S/cm.

Objectives

This research was initiated to investigate synthesis of improved polymer electrolytes for lithium-ion battery applications. The overall goal of this effort was to demonstrate that the enzyme-catalyzed polymerization route is practical and efficient. To achieve this goal and to justify the transition into the second Phase of this work, the following specific objectives needed to be accomplished:

- Demonstrate feasibility of the polymer synthesis where the phenol repeat unit is substituted in the *para* position with short PEO segments.

- Characterize the polymer in terms of thermal and electrical properties.

- Establish electrolyte characteristics of the polymer/lithium salt complex by measurement of its electrical characteristics.

- Demonstrate the possibility of fabricating nanocomposites with clays for improving mechanical, thermal and interfacial stability.

- Demonstrate the high room temperature conductivity of the best composition in terms of processing, manufacturability and mechanical integrity.

- Demonstrate the polymer electrolyte performance in a laminated Li-ion battery design.

Approach

Our approach combines various aspects toward the synthesis of the novel polymer electrolyte. *The first aspect* deals with the use of short chain PEG in order to avoid crystallization and increase of T_g of the final product. As mentioned above, this will allow the use of the polymer in lithium-ion batteries in a wide temperature range. *The second aspect* concerns the covalent bonding of these short PEG segments onto a monomer which typically results in a thermally stable backbone. The monomer chosen here is phenol in order to take advantage of *third aspect*, which consists of the polymerization of PEG-phenol monomer *via* enzyme catalysis as a follow up on the work developed at Natick RD&E Center which uses enzyme-catalyzed reactions for the synthesis of aromatic polymers. In their work, Ayyagari *et al.* {4} have synthesized and characterized substituted phenol polymers obtained *via* horseradish peroxidase (Type II) (abbreviated as HRP) catalyzed polymerization in various media. The synthesis route is shown in **Fig. 1** for illustration purposes.
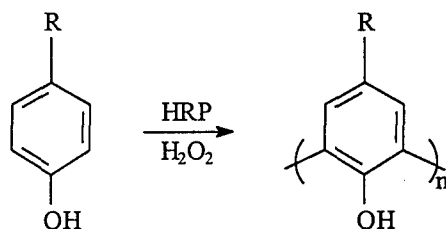
R = ethyl, phenyl

Fig. 1: Schematic of Phenol Polymerization Catalyzed by Horseradish Peroxidase (Ref. 3)

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In our approach, the phenol monomer is substituted in the *para*-position with a short PEG. Based on the intrinsic electrolytic properties of PEG, eight repeat units are enough to provide the interfacial characteristics needed for efficient Li$^+$ diffusion. However, shorter segments might be enough when anchored to another polymer repeat unit such as phenol. The polymer having phenol as the repeat unit is polycrystalline in nature. When substituted with an aliphatic group, the amorphous character is enhanced. Therefore, an optimal segment length of the PEG needed to be used such that the resulting polymer is mostly amorphous. The appropriate segment length has been narrowed down during the Phase I, and will be optimized further during the Phase II effort. The structure of the optimized polymer electrolyte as a result of the Phase I work is shown above in **Fig. 1** with

$$= -\!\!\left(\!\!- O \ CH_2CH_2 \!\!-\!\!\right)_{\overline{m}} O$$

(m = 8-16, which corresponds to a PEG segment molecular weight of 350-700).

As an extension to this approach, a plasticizer component will also be attached covalently to the aromatic repeat unit in Phase II. An excellent plasticizer would be a sulfonate group which will substitute the hydroxyl group *via* conventional sulfonation reactions once the polymerization reaction is completed. In addition to facilitating the Li$^+$ diffusion, the sulfonate group provides a better wetability for the electrodes. The structure of the modified polymer electrolyte is shown in **Fig. 2**.

$$R = -\!\!\left(\!\!- O \ CH_2CH_2 \!\!-\!\!\right)_{\overline{m}} O$$

M = H, Li, Na, etc.
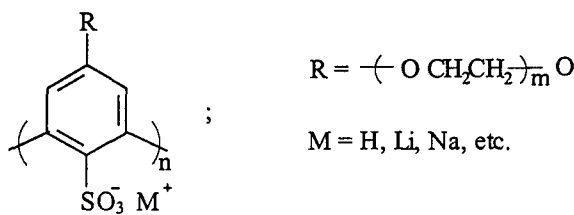
Fig. 2: Schematic Structure of the Proposed Polymer Electrolyte

As a lithium salt, we have used the experimental lithium trifluoromethansulfonimide of the formula LiN(CF$_3$SO$_3$)$_2$, considered as one of the most stable lithium salts with high conductivity in a wide temperature range, and is marketed as *HQ-117* by *3M Co.*

The last but not least important component of our devices is the current collector. We have adopted the technology used by the leading manufacturer of advanced electrochemical capacitors, which consists of using a thin (25μm) highly conductive elastomer as our conductive substrate. The latter is laminated to the anode and cathode, which are separated by the electrolyte layer to result in a highly flexible, and compact laminated battery sealed at the edges *via* the elastomer outer layers. Besides these added characteristics, corrosion encountered with most metallic current collectors is being avoided here. This effort is being carried out in collaboration with Evans Capacitor Co., who would be more involved in the Phase II program.

In the second part of our approach, we have used the polymer synthesized above, with the best ionic conductivity, in a sol gel process, which resulted in a high quality solid-state polymer electrolyte. The fluid PEG segments facilitate lithium ion transfer with no detectable decomposition based on the cycling measurements performed in the lithium battery assembly. As a part of this process, within smectite clays such as lithium montmorillonite was used to provide nanoscale building blocks for intercalation of the reacted polymer/sol gel species. *The combination of such layered inorganic materials with the sol-gel process has been used here for the first time and enhances the overall characteristics of the polymer electrolyte.*

The resulting solids should be highly organized and highly microporous as the clay layers are propped apart by the polymer electrolyte pillars. The pillaring process helps prevent the collapse of the clay layers and paves the way to a more organized intercalation of the lithium salt characterized by a high ionic conductivity and a high lithium transference number (bulky anion). The polymer/lithium is expected to be intercalated within the clay galleries in an orderly fashion and this will be investigated during the Phase II program using X-ray diffraction. The sol gel electrolyte species intercalated between the clay layers can be conceptualized as shown in **Fig. 3**.
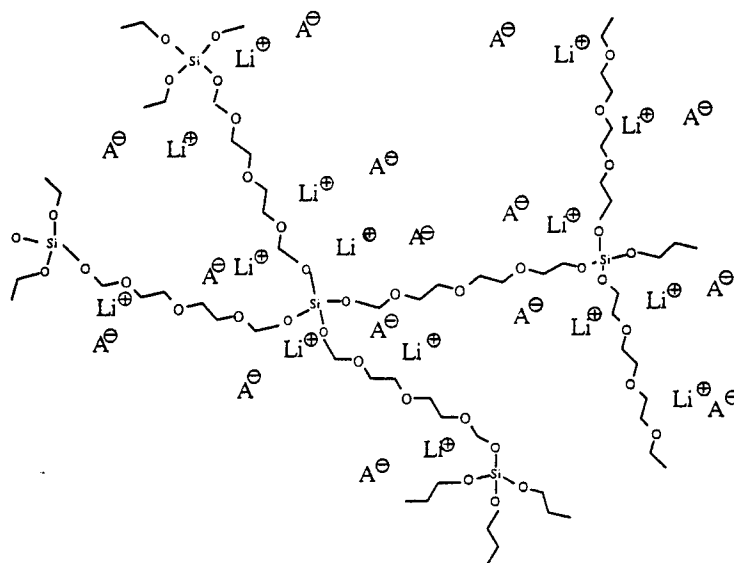
Fig. 3: Interconnected Network of the So Gel Polymer Electrolyte

The silicate species bind several PEG segments to create a network, thus enhancing PEG's capability of facilitating lithium ion mobility and thermal and mechanical properties of the electrolyte overall. Thus, lithium ions can move freely within this network, while the bulky sulfonimide anion is being held back due to its slow diffusion. This effect is highly desirable in polymer electrolytes, where the Li^+ mobility is maximized and that of the anion is minimized. This is referred to, as "Li^+ transference number".

Preliminary testing of the resulting polymer electrolyte, obtained by enzyme-catalyzed polymerization, in a laminated battery design has been carried out, using $LiCoO_2$ and $LiMnO_2$ as cathode materials and a lithium anode. *Advantages* of this approach consist of:

- Ability to control the polymer electrolyte's molecular weight and distribution through enzyme-catalyzed polymerization.

- Ability to control the molecular weight of the PEO segment and the percentage of grafting onto the main aromatic backbone, and therefore, the T_g of the resulting polymer.

- Ability to induce processability by varying the length of the PEG segment.

- Ability to enhance thermal, chemical and electrochemical stability of the polymer through fluorination of the aromatic ring and/or fabrication of nanocomposites with ordered clays and/or through the sol gel process.

- Ability to fabricate high conductivity polymer electrolytes with good interfacial characteristics with both the lithium or lithium-ion anode and the cathode.

- Ability to fabricate batteries with versatile designs due to the flexibility of the different components, particularly, the electrolyte and the current collector, with the latter being low cost, light weight and outstanding anticorrosion properties.

Results and Discussion

Synthesis of the Phenol Monomer Derivative

We have used two routes for the synthesis of the monomer necessary to achieve the proposed polymer electrolyte using enzyme catalysis. Since PEO or PEG are well known ionic conductors, we have chosen to derivatize the phenol monomer with such ether linkages whose chain length is above what is needed for the resulting compound to have a strong ionic character (≥ 8 -CH_2CH_2O- units). The polyether chain length should be however low enough so that crystalline regions do not form, and that a largely amorphous character is maintained. For this reason, we have chosen a PEG with a molecular weight of 350-750 for the derivatization of phenol. From previous experiments, a PEG with a molecular weight of 400 is considered as a good ionic conductor.

The reaction schemes used to synthesize the phenol derivative from commercially available constituents are as follows and are shown in **Fig. 4**:

Step 1. The starting phenol compound, 4-hydroxyphenylacetic acid, is reacted with N-hydroxysuccinimide (HONSu) and dicyclohexylcarbodiimide (DCC) in ethyl acetate at 0°C as shown below {5}.

Step 2. PEG methyl ether with a M_w of 350, 550 or 750 (Aldrich) is reacted with tosyl chloride in THF to yield the PEG tosylate derivative. The latter is then reacted with sodium phthalimide in methylene chloride. The resulting material is converted to the amino derivative using hydrazine in ethanol. These reaction sequences are shown in schemes 2 through 4 {6}.

Step 3. The imide derivative of phenol obtained in reaction (1) is added to the PEG amine derivative obtained in reaction (2) to yield the desired phenol with the *para*-polyether linkage as shown in reaction scheme (5). The polyether chain comprises approximately 8, 12 and 16 ethylene oxide repeat units in the PEG 350, 550 and 750 respectively. All three are amorphous materials, yet have in principle a sufficient number of oxygen atoms for transferring the lithium ion efficiently.

We have confirmed the structure of the monomers obtained in reaction scheme (5) by chromatography before proceeding with polymerization.

Polymerization of *p*-PEG-Phenol Monomer

The phenol derivatives prepared according to the procedures described above were polymerized using two different media according to procedures described by Akkara *et al.* {3,4} shown earlier in Fig. 1.

Because this type of monomer is readily soluble in water, the reverse micelle preparation technique was not necessary. Therefore, the synthesis was carried out in an aqueous medium with a pH of 7, which was achieved using the buffer tris(hydroxymethyl)aminomethane-HCl (0.5 M). The appropriate amount of the enzyme HRP was added to the monomer solution. After stirring for complete dissolution and homogeneity, hydrogen peroxide (30% solution) was added drop-wise into the reaction vessel. An immediate change of color is observed upon addition of the peroxide, however, to ensure completion of the reaction, the mixture was allowed to react overnight. The resulting polymer and the buffer are soluble in water, and therefore purification by precipitation in a non-solvent for the buffer was necessary to

isolate the polymer. The resulting material was collected by evaporation of the solvent. The polymer consisted of a gel with a slight yellow color.
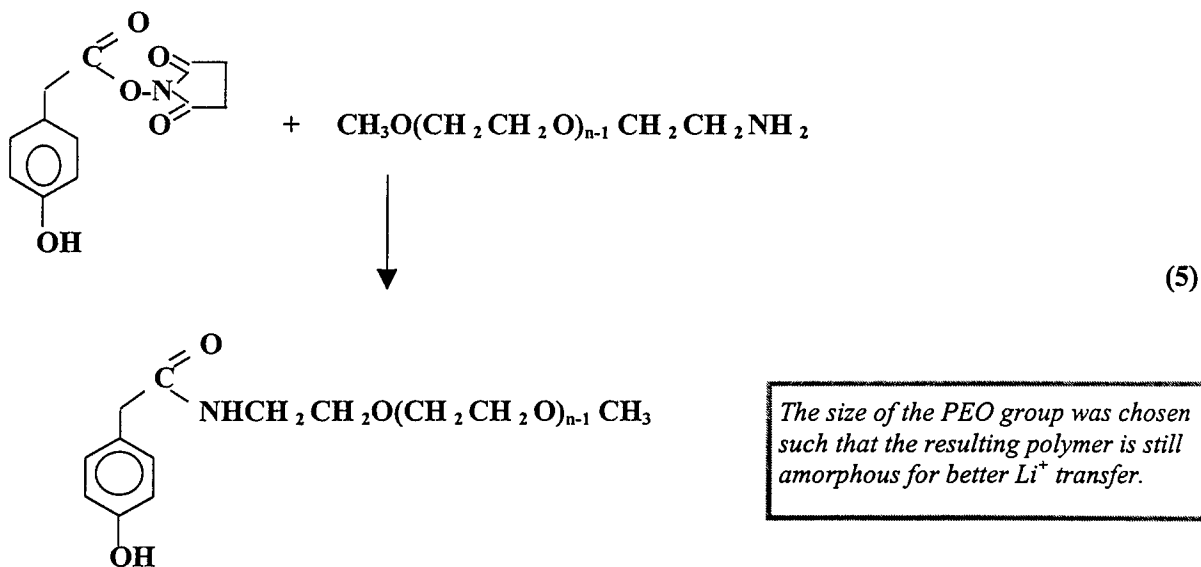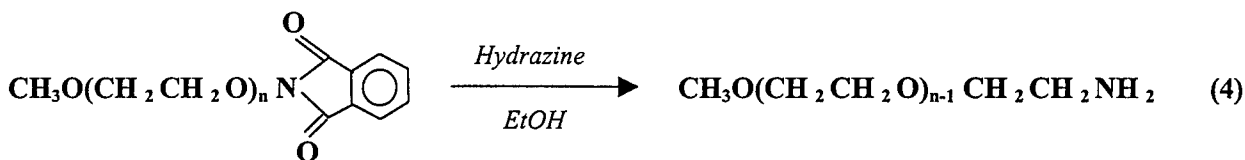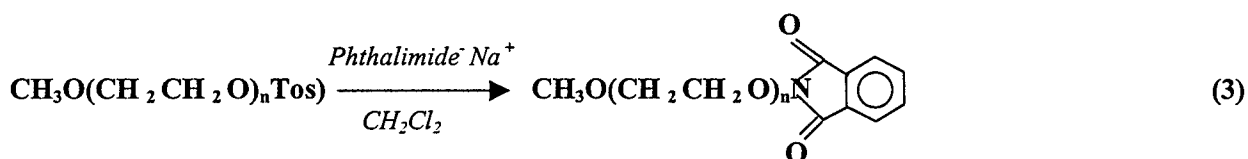

$$CH_3O(CH_2CH_2O)_nH \xrightarrow[THF]{TosCl} CH_3O(CH_2CH_2O)_nTos \quad (2)$$

$$CH_3O(CH_2CH_2O)_nTos) \xrightarrow[CH_2Cl_2]{Phthalimide^-\ Na^+} CH_3O(CH_2CH_2O)_n N \quad (3)$$

$$CH_3O(CH_2CH_2O)_n N \xrightarrow[EtOH]{Hydrazine} CH_3O(CH_2CH_2O)_{n-1}CH_2CH_2NH_2 \quad (4)$$

+ $CH_3O(CH_2CH_2O)_{n-1}CH_2CH_2NH_2$

(5)

C=O NHCH$_2$CH$_2$O(CH$_2$CH$_2$O)$_{n-1}$CH$_3$

The size of the PEO group was chosen such that the resulting polymer is still amorphous for better Li$^+$ transfer.
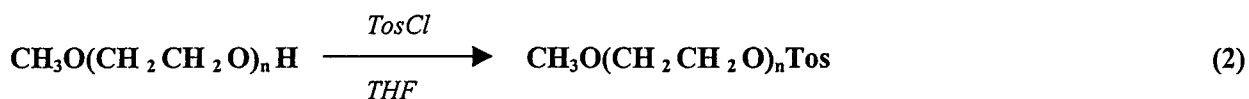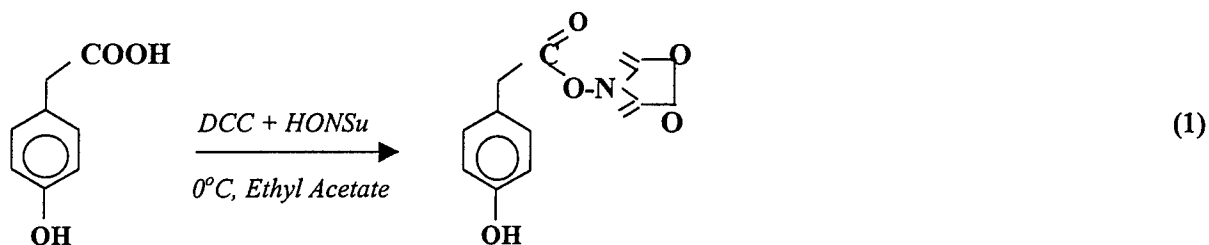
Fig. 4: Reaction Sequences for the Preparation of the PEG-Phenol Monomer

The second medium used consisted of dioxane/water mixture (80/20) in which the monomer is readily soluble as well. The polymerization procedure is the same as in the aqueous medium. The resulting polymer was collected using the procedure mentioned above. Unlike the one prepared in the aqueous medium, this polymer consisted of a lower viscosity gel than the previous preparation. This is indicative of lower molecular weights.

In addition to the PEG-phenol homopolymers, we have prepared two copolymers where the comonomer is *p*-ethoxyphenol and *p*-phenylphenol known to undergo polymerization individually as described in references 3 and 4. Because these two monomers are insoluble in water, the dioxane/water mixture was used as the polymerization medium. The copolymers were prepared using similar conditions to those used for the PEG-phenol homopolymer, with a comonomer molar ratio of *1:1*. The resulting materials in both cases consisted of a low viscosity gel similarly to that of the homopolymer prepared in the same medium. Here again, a low molecular weight is probably the cause of such morphology.

The first route used to synthesize the PEG-based polymer electrolyte through enzyme catalysis involved the synthesis of the PEG-phenol monomer first then polymerization *via* HRP catalysis. *The second method* we have investigated, consists of polymerization of the phenol derivative *via* HRP catalysis, then substituting the phenol repeat unit in the polymer with PEG-based segments. For this purpose, we have used aminophenol as the starting material. This monomer has been successfully made using a 75/25 volume ratio of dioxane/water as the polymerization medium, and HRP/hydrogen peroxide as the catalyst. The resulting polymer is then reacted with an ester of methoxypoly (ethylene glycol) modified lysine available from Shearwater Polymers (referred to as *PEG2-NHS*), which has the structure shown in **Fig. 5**:
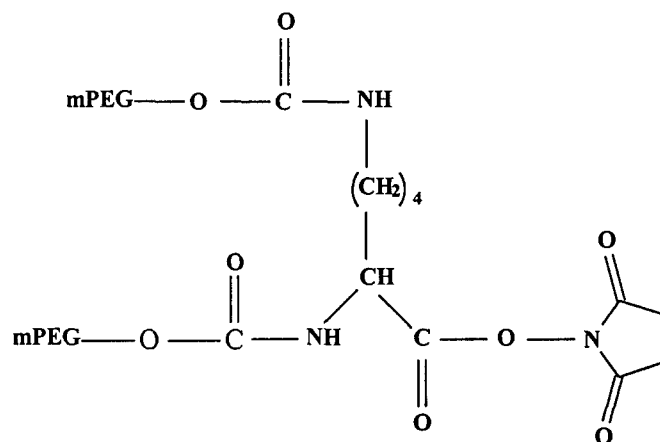

Fig. 5: Structure of the Double-Branched PEG2-NHS

The molecular weight of the PEG segment in each branch is 5000, which results in a total molecular weight of the modified lysine of 11,136. Because the ionic conductivity properties are intrinsic to the PEG segment, the 5000 molecular weight is well suited for our application. This compound melts at 59°C according to our differential scanning calorimetry (DSC) measurements. Following reaction with poly(aminophenol), an endothermic peak at 56.8°C was obtained in the DSC and corresponds to the melting point of the PEG-aminophenol copolymer. The melting point remains practically unchanged. This might be due to the structural characteristics being dominated by the PEG portion. Further characterization of the synthesized polymer was not pursued due to its insolubility in water or common organic solvents. It is suspected that substitution of the aminophenol repeat unit was too small using this synthesis route.

Sol Gel Electrolyte Preparation

Sol gels seem to be the most promising electrolyte materials from all aspects of this research. They are simple to synthesize from cheap, commercially available materials, and comprise tetraethoxysilane (TEOS), the PEG synthesized as described in the previous sections, lithium salt. In our proprietary formulation, a lithium montmorillonite is added for ordering purposes and an added mechanical integrity. To this formulation, we added lithium aluminate (γ-LiAlO$_2$) to improve the interfacial stability between the electrolyte and the lithium anode.

TEOS and water were sonicated together for one hour. Our PEG and the lithium salt *HQ-117* mixture (O/Li = 8/1) was added to the mixture and sonicated for an additional hour. The sol gel mixture at this point is a cloudy liquid with the PEG phase partly separated from the silicate phase. A small amount of 1M HCl was added to the sol gel to give a single-phase cloudy solution, and continued sonication for another hour. The sol gel was cast in a Teflon-coated dish and heated in a vacuum oven at 100°C for several hours. The sample was then taken out of the oven once it cooled down to room temperature. Translucent flexible films resulted from this process.

Polymer Electrolytes based on Solvent-Free Gels

Poly(ethylene glycol) methacrylate with an average molecular weight of 360 was polymerized in the form of a gel using the appropriate amounts of monomer, ammonium persulfate and N,N,N',N'-tetramethylethylenediamine (TEMED) in water. The monomer's structure is such that there are six repeat units of PEG. Therefore, the polymer resulting from this step alone is expected to yield a reasonable ionic conductivity due to the inter-connected network of the gel, and therefore, the reasonably good interaction between the PEG segments. We have characterized the gel using electrochemical impedance spectroscopy to determine the conductivity of the polymer gel alone and when combined with the lithium salt used in all our experiments. This work was initiated for versatility reasons, and will be combined in the Phase II program with the PEG-phenol polymer obtained *via* enzyme catalysis. Our plan will be to form the methacrylate gel in the presence of our polymer so that the latter is incorporated in the gel's network.

Characterization

Structural Characterization

The structure of the polymers obtained *via* enzyme catalysis was investigated by proton NMR (Xerox Research Center, Missisauga, Ontario) in CDCl$_3$/TMS. A characteristic spectrum of a *p*-PEG-phenol polymer, where the PEG segment has a molecular weight of 550 is shown in **Fig. 6**. The dominant peaks centered at 3.65 ppm correspond to the protons of the PEG segments. The two protons of the phenol repeat unit (in the *meta* position *vis-à-vis* the PEG group) are characterized by a shift at 6.7 and 7.2 ppm as can be seen in the insert (X 64). Due to the low intensity of the aromatic protons compared to those of PEG, integration was difficult. The PEG polymer obtained from Shearwater Polymers in which each PEG segment has a molecular weight of 5000 was used as a reference for the peaks observed in our polymer. **Fig. 7** shows the spectrum of *PEG2-NHS* in which the PEG protons are observed at the same shift found for our polymer (3.65 ppm). The insert of the latter figure (X 128) shows the rest of the peaks, which correspond, to the remaining protons in the structure. It is important to note that a water peak (1.9 ppm) is found in the *PEG2-NHS* while this peak is absent in our polymer. This could be due to the hydrophobic nature of the phenol repeat unit, which is a desirable property in an electrolyte system intended for use in lithium ion batteries.

The molecular weight of the above polymer was determined using GPC with polystyrene being the standard at Xerox Research Center. The measurement, in the same solvent as for NMR (CHCl$_3$), yielded a
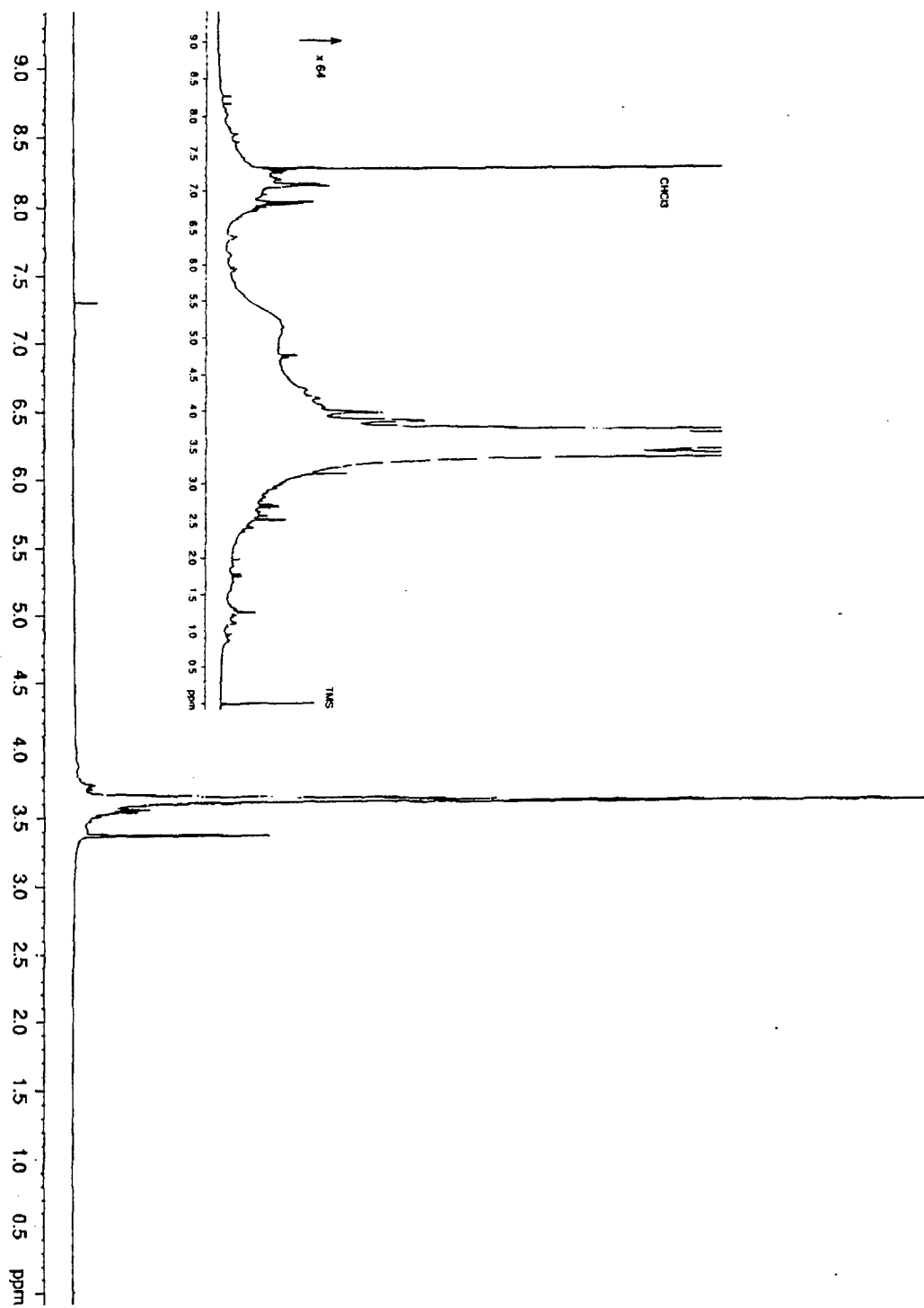
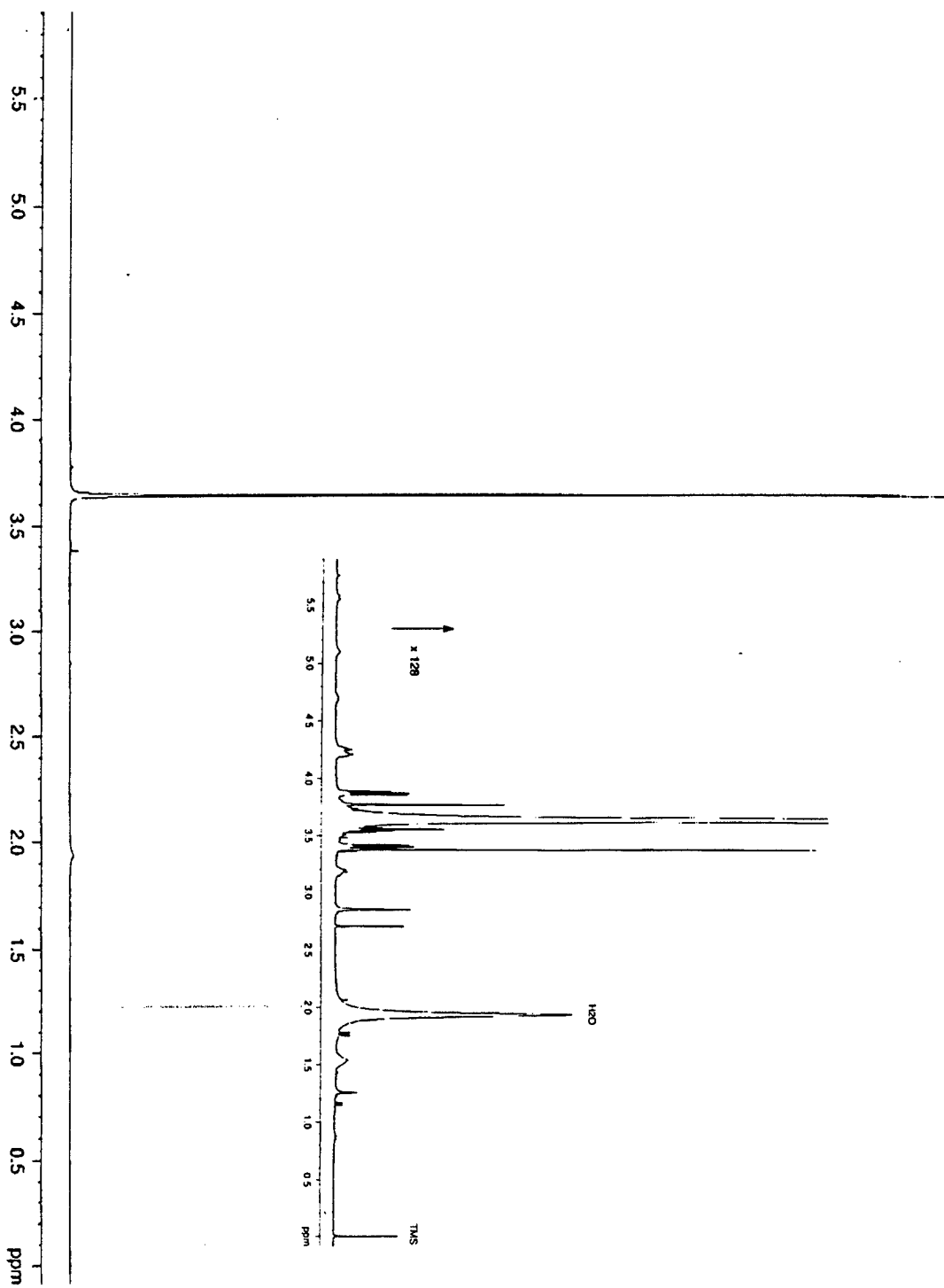**Fig. 6: Proton NMR of the PEG 550-Phenol Polymer**

Fig. 7: Proton NMR of the Shearwater Polymers' PEG2-NHS

molecular weight of 8963 (measurements performed at Xerox research Center). This corresponds to approximately 13 repeat units of the PEG-phenol monomer whose structure was shown earlier. The PEG portion constitutes 80% of the molecular weight, and therefore, such a polymer is structurally ideal for ionic conduction.

Thermal Properties

Thermogravimetric analysis (TGA) was conducted on our 550 polymer. The result is displayed in **Fig. 8**. The polymer exhibits an excellent stability, with no decomposition before 215°C. DSC (**Fig. 9**) was performed as well. Although the baseline is not very good, one can observe several broad peaks corresponding to exothermic reactions from -30°C to 22°C. These features are typically observed in amorphous PEG and correspond glass transition that is not well defined, but is characteristic of the fluidity of the PEG segments. The exothermic peaks observed at higher temperatures correspond probably to the softening of the PEG-phenol copolymer segments. An endothermic peak, not clearly assigned at this point, is observed at 25°C, and another at 72°C, which corresponds to the melting point of the PEG-phenol polymer, similarly to what was obtained by capillary tubing melt temperature measurement. This is encouraging since the fluidity of the PEG segments is necessary for ionic conduction, while the rigidity of the backbone is required for thermal stability of the electrolyte system. Such fluidity will be demonstrated in the battery characterization section at temperatures below RT. TGA and DSC were obtained at Illinois State Univ., Normal, IL, as well as at Xerox Research Center.

Transport Properties

The various polymers were characterized using the 4-probe technique and electrochemical impedance spectroscopy (EIS) (CH Instruments Electrochemical Workstation Model 660A) to determine their ionic conductivity. In **Fig. 10 a**, the substrate consists of a highly polished alumina, coated (by evaporation) with 4 equidistant strips of gold. The width of each strip is 1 mm and the separation between two neighboring strips is 5 mm. In **Fig. 10 b**, Films were cast and sandwiched between titanium nitride (TiN)-coated stainless steel (SS) blocking electrodes.
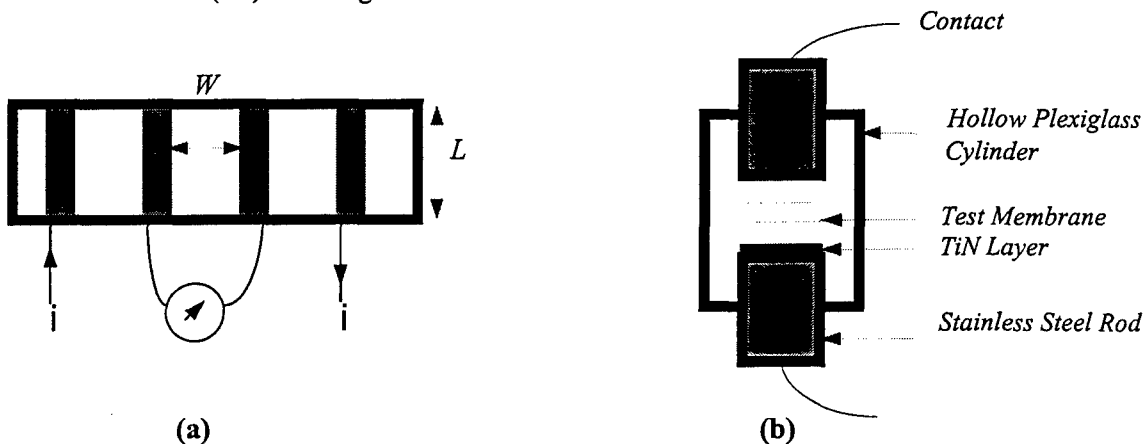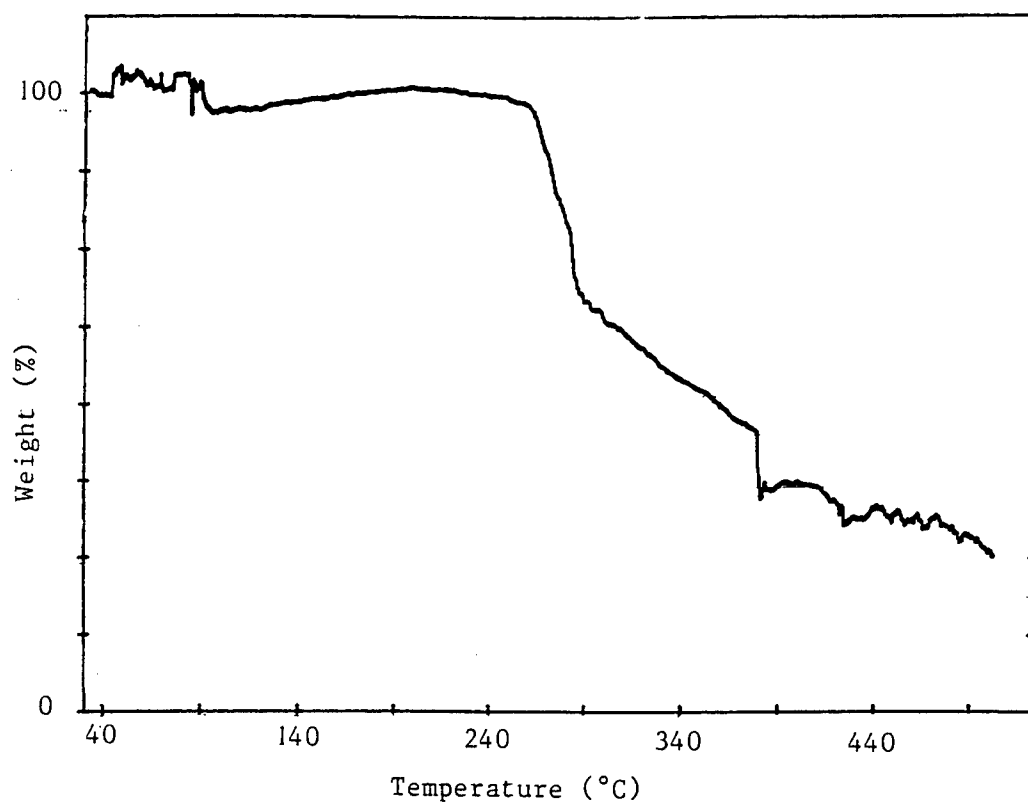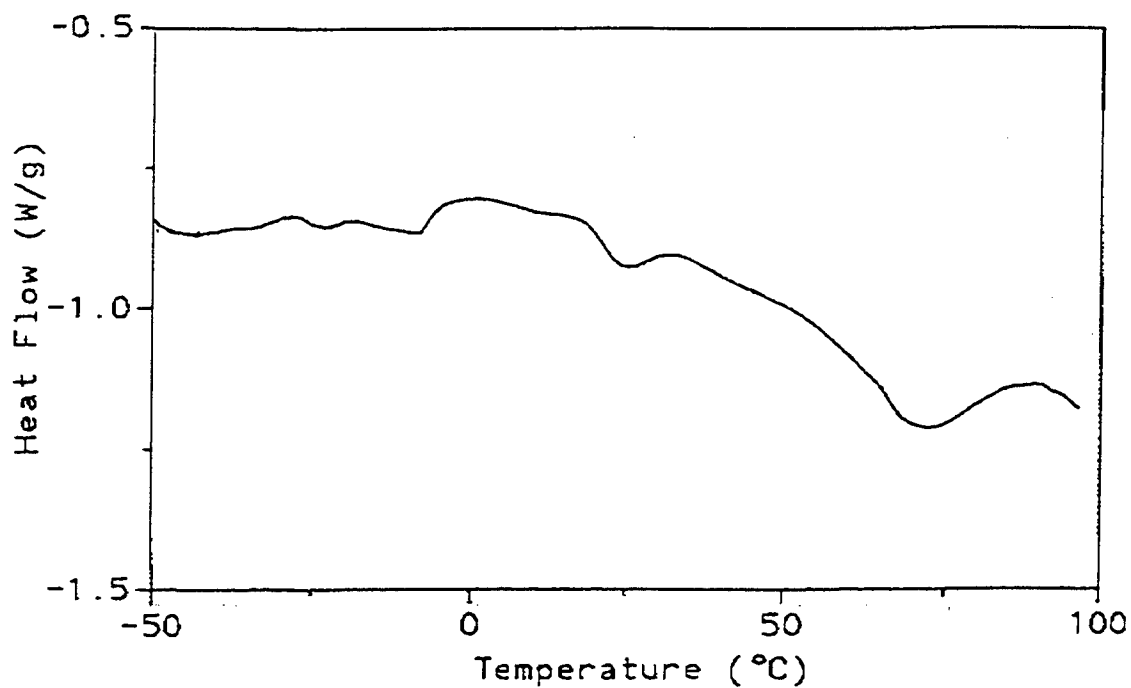

(a) **(b)**

Fig. 10: Schematic of the Four-Probe (a) and Two-Electrode (b) Conductivity Measurements

The first technique was used for comparison purposes and conductivity was calculated using the equation:

$$\sigma = \frac{1}{R} \cdot x \cdot \frac{L}{W \cdot x \cdot T}$$ in $(\Omega cm)^{-1}$; or S/cm, where L = length, W = width, and T = thickness;

Fig. 8: Thermogravimetric Analysis Spectrum of the PEG 550-Phenol Polymer

Fig. 9: Differential Scanning Calorimetry of the PEG 550-Phenol Polymer

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However, most of our measurements used the second technique because it provides other electrochemical characteristic besides ionic conductivity values. EIS measurements were run between 0.01 or 0.1 and 10^5 Hz. An ideal equivalent circuit of the TiN/polymer/TiN cell is shown in **Fig. 11** for illustration purposes:
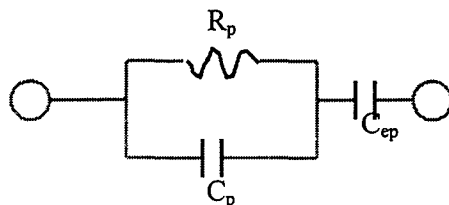
Fig. 11: Equivalent Circuit of the Electrochemical Cell of Figure 10 b

where R_p and C_p denote the polymer electrolyte bulk resistance and capacitance respectively, and C_{ep} represents the double-layer capacitance at the electrode-electrolyte interface.

According to this ideal circuit, a theoretical impedance spectrum represented by the Nyquist plot, which consists of a semicircle toward the high frequency and a vertical spur at the low frequency section. Departure from a vertical spur can be explained by the coexistence of several diffusion mechanisms of ionic species in the bulk of the electrolyte. Curvature of the low frequency section represents a cavitation phenomenon, which can be explained by the diffusion of ionic species towards the electrodes, and this is of course desirable in battery or capacitor applications.

Conductivity is calculated using the relation given below:

$$\sigma = \frac{1}{Rp} \cdot x \cdot \frac{T}{A},$$ where T (cm) is thickness of the polymer film, A (cm^2) is its area, and σ is in S/cm.

The resistance is determined from the intersection points of the semicircle with the X-axis, and in the absence of a clear semicircle, the resistance is taken from the intersection of the curve with the X-axis at the high end of the frequency range studied.

Homopolymer and Copolymers of the PEG Phenol Monomer: In **Fig. 12**, we have plotted the impedance data represented by Nyquist plots for the homopolymer and its two copolymers. Conductivity decreases in the following order: homopolymer > ethoxyphenol copolymer > phenylphenol copolymer. The values are 10^{-5}, 2×10^{-6}, and 9×10^{-7} S/cm respectively. These values are due in part to the increase in distance and therefore decrease in interaction between the PEG segments in the copolymers. The difference between the ethoxyphenol copolymer and the phenylphenol copolymer can be explained by the fact that the ethoxy group is of the same nature as the PEG segment and can therefore contribute to lithium ion motion. However, in both cases, in addition to the separation of the PEG segments by other species, the molecular weight is probably lower than in the homopolymer as mentioned above and as was observed from their morphologies. Furthermore, cavitation of the ionic species toward the electrodes seems to be strong in the homopolymer. The same data is shown in **Fig. 13** in the form of phase angle shift *vs.* frequency. A perfect resistor will have a maximum angle shift of -45°. A deviation from this maximum towards lower angles as is the case for the phenylphenol copolymer indicates a poor ohmic behavior. From this data, it appears that the homopolymer and the ethoxyphenol copolymer seem to have the right behavior. A shift of the maximum position towards higher frequencies indicates conductivity by bulkier ionic conductors. This is the case for the homopolymer whose phase angle shift reaches a maximum of -43° at 2 Hz, while the ethoxyphenyl derivative reaches a maximum of -48° at 0.5 Hz. These results are consistent with the structural characteristics of the three polymeric systems studied here.
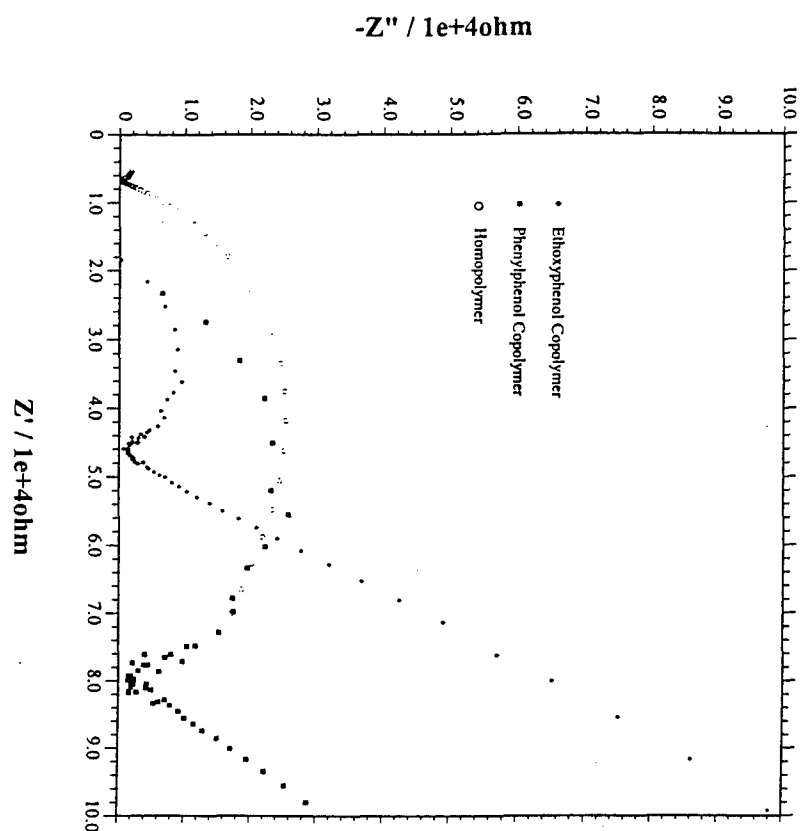
-Z" / 1e+4ohm

- Ethoxyphenol Copolymer
- Phenylphenol Copolymer
○ Homopolymer

Z' / 1e+4ohm

Fig. 12: Nyquist Plots of the PEG-Phenol Polymer and itsCopolymers
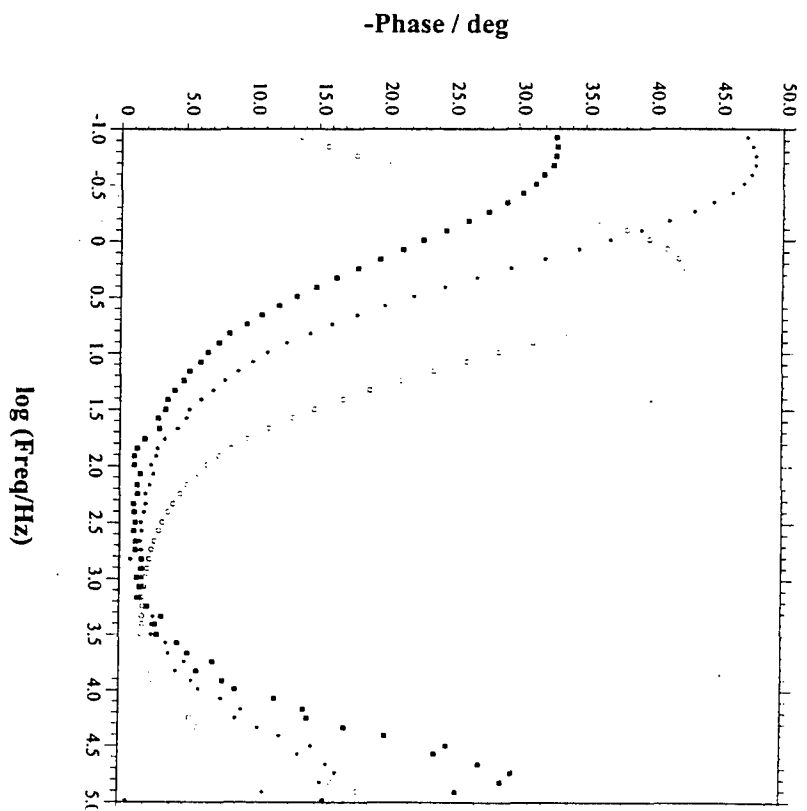
-Phase / deg

log (Freq/Hz)

Fig. 13: Current-Voltage Phase Angle Shift of PEG-Phenol Polymer and its Copolymers

This does not mean that copolymers should be ruled out, because their ionic conductivity and their overall properties depend on the comonomer ratio and the length of the PEG segment. These two parameters are inter-related, and such experiments are beyond the scope of this study. Because the copolymers made using the PEG-phenol derivative in combination with ethoxy- and phenyl phenol comonomers using a 1:1 ratio yielded lower ionic conductivity than that of the PEG-phenol homopolymer, we decided at this stage to proceed with the latter material for further electrolyte related studies. Depending on their conductivity, the best homopolymer in terms of the PEG segment molecular weight will be chosen for further work including a combination of two of these materials. The latter approach will be optimized in the Phase II program. The PEG-phenol polymer where the PEG segment has a molecular weight of 350 and 750 were evaluated as well. As far as impedance analysis and conductivity measurements go, the 550 polymer has a higher conductivity than the 350 by approximately 5 times as can be seen from the Nyquist plots shown in **Fig. 14**. However, there was practically no difference between the 550 and 750 polymers, and therefore, any of the latter two derivatives is a potential candidate as a polymer electrolyte, but a 350 polymer in a sol gel matrix as explained in the "approach" section should work well.

Lithium Salt/Polymer Electrolyte Complex: **Fig. 15** shows the Nyquist plots for the homopolymer and a mixture of the homopolymer with the high Li^+ mobility salt, lithiumtrifluorosulfonimide (3M). The mixture is made in solution, since both components are water soluble, for homogeneity purposes. The ratio is such that the O/Li ratio is 1/8. This ratio has shown the best performance in terms of Li^+ conduction in PEO-based electrolytes. The conductivity value obtained from the plot of the lithium salt blend is 8×10^{-4} S/cm, which represents an increase of almost two orders of magnitude compared to the pure homopolymer. A conductivity approaching 10^{-3} S/cm is considered as a major advance in this area. **Fig. 16** shows the phase angle shift *vs.* frequency of the above data. The maximum shift (-43°) is similar for the homopolymer with and without the lithium salt, indicating good resistor/conductor properties. However, and as expected, the maximum is shifted slightly from 2 Hz to 5 Hz due to the interaction of lithium ions with the PEG oxygen atoms, thus making it look bulkier species. The shoulder, which represents a maximum at 100-200 Hz, is probably due to the low mobility of the bulky sulfonimide anions. This latter effect is desirable since the lithium ion motion is the one that is needed in the direction of the anode, and this of course should result in an increase of the lithium ion transference number.

Sol Gel Polymer Electrolyte: A sol gel polymer electrolyte formulation consisting of the components mentioned in the "approach" section and based on the 550 polymer synthesized in this work was also studied. The lithium salt is the same as that used with the homopolymer studied above. **Fig. 17** shows Nyquist plots of the material at 0V and when 1 V and 2 V are applied to the TiN/Electrolyte/TiN cell. Conductivity, determined from the first semi-circle becomes higher with the increased voltage, correspond to an ohmic behavior, with a value at no bias being approximately 5×10^{-4} S/cm. This is similar to what was obtained earlier with the homopolymer/lithium salt combination (8×10^{-4} S/cm). In addition to the increase in ionic conductivity with voltage, which is a phenomenon that is necessary for battery operation, cavitation is increased as expected here again. The phase angle shift of this sol gel formulation is compared to that of the homopolymer shown earlier in Fig. 16 since the same polymer is used in both formulations. This data is shown in **Fig. 18**. A slight downward shift of the maximum for the sol gel is obtained. This is due to the confinement of the PEG segments by the silicate species *via* covalent bonding. Furthermore, and this is quite interesting, the shoulder which corresponds to the bulky anions observed in the case of the homopolymer electrolyte, is absent in the sol gel plot. High lithium ion transference numbers should result from such a formulation. The phase angle shift (**Fig. 19**) decreases as the voltage is increased. This is indicative that the current and voltage become closer to being in phase as is observed for the case when a 2 V bias is applied. This means that the current is being produced due to the lithium ion mobility alone rather than that of the ion plus the ion-lattice interaction. Charge/Discharge cycles were conducted using chronoamperometry and chronopotentiometry as shown in **Fig. 20** (10 and 25 cycles respectively). The symmetric character of these curves is due to the symmetric construction of the cell. Charge and discharge times are similar due to this reason and the homogeneity of the electrolyte.
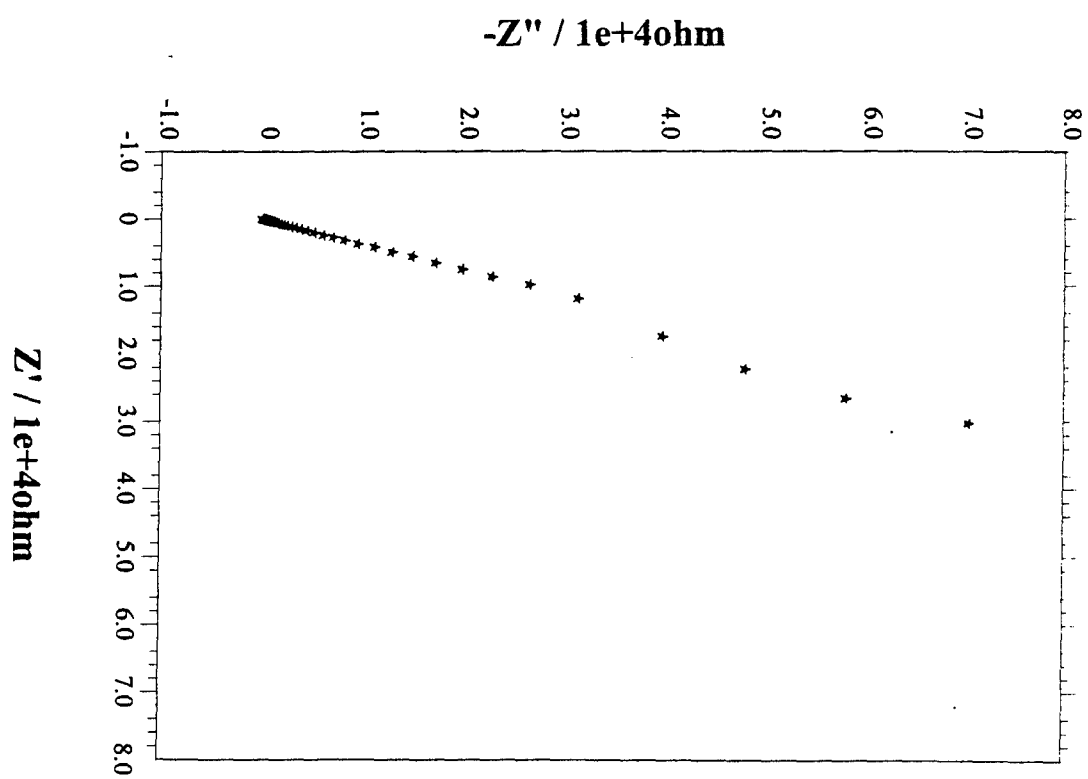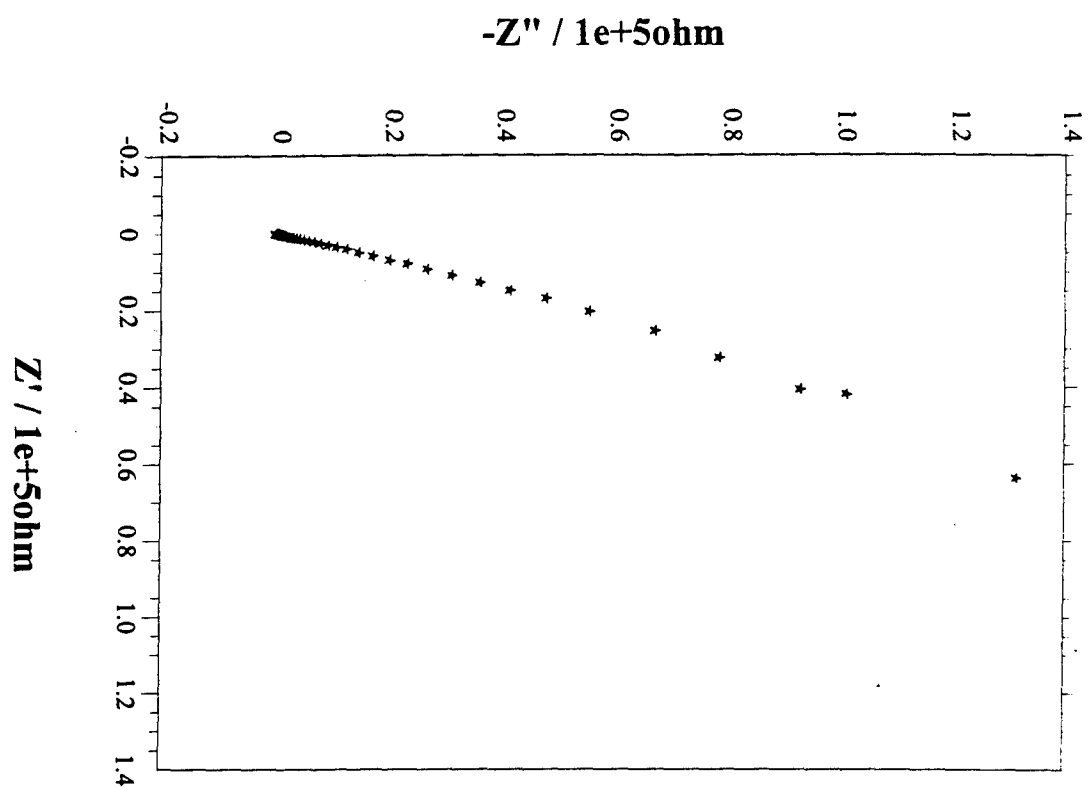
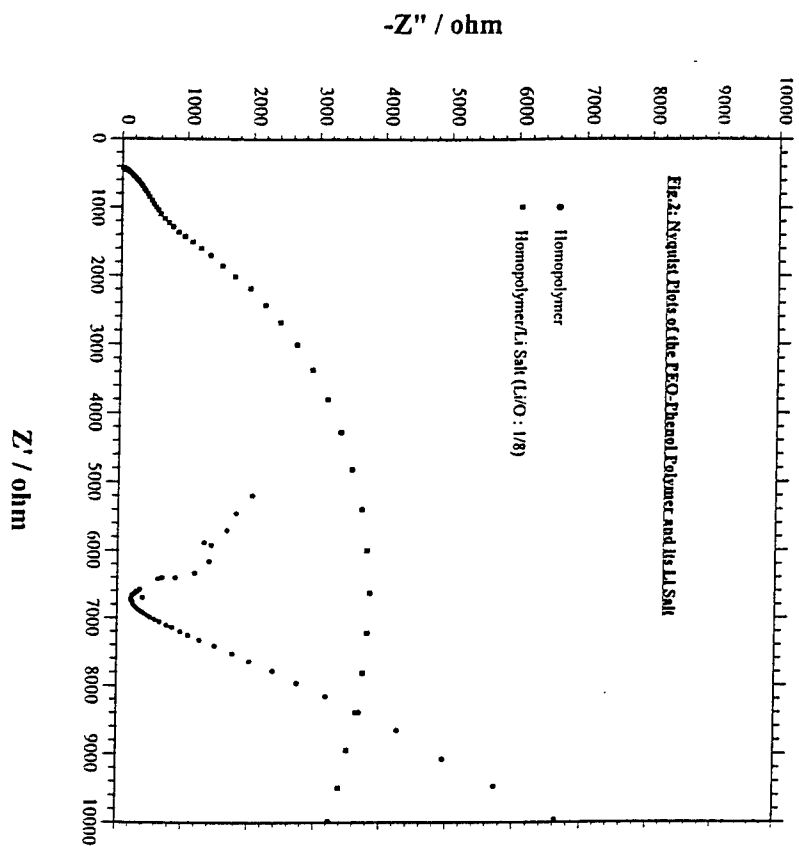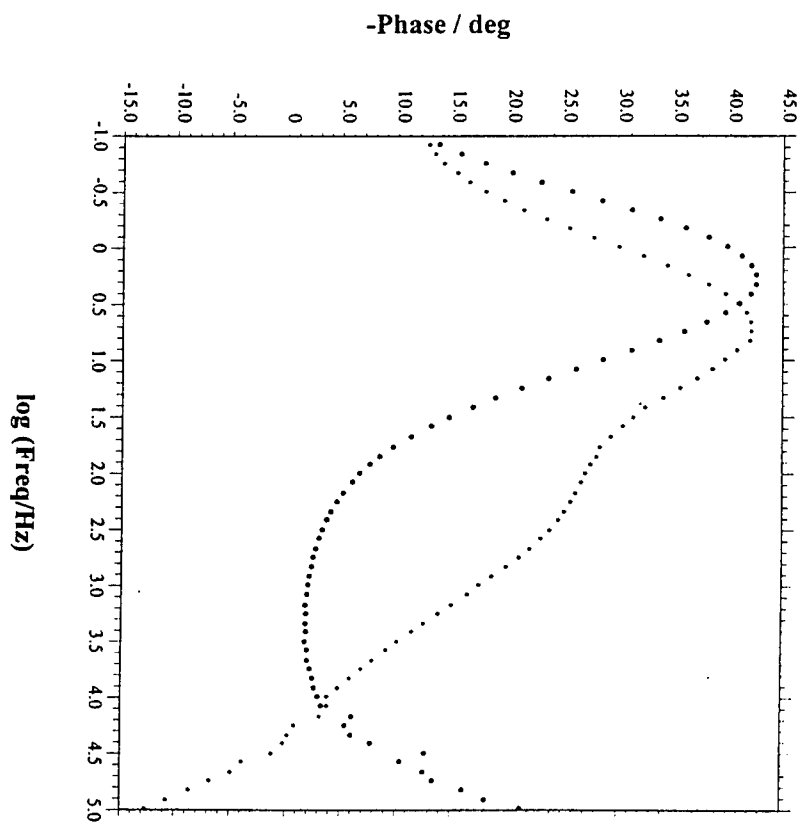Fig. 14: Nyquist Plots of the PEG 350-Phenol Polymer (*left*) and PEG 550-Phenol Polymer

Fig.2: Nyquist Plots of the PEO-Phenol Polymer and its Li Salt

-Z" / ohm

- Homopolymer
- Homopolymer/Li Salt (Li/O : 1/8)

Z' / ohm

Fig. 15: Nyquist Plots of the PEG-Phenol Polymer (•) and its Lithium Salt Complex (■)

-Phase / deg

log (Freq/Hz)

Fig. 16: Current-Voltage Phase Angle Shift of PEG-Phenol Polymer (•) and its Lithium Salt Complex (∗)
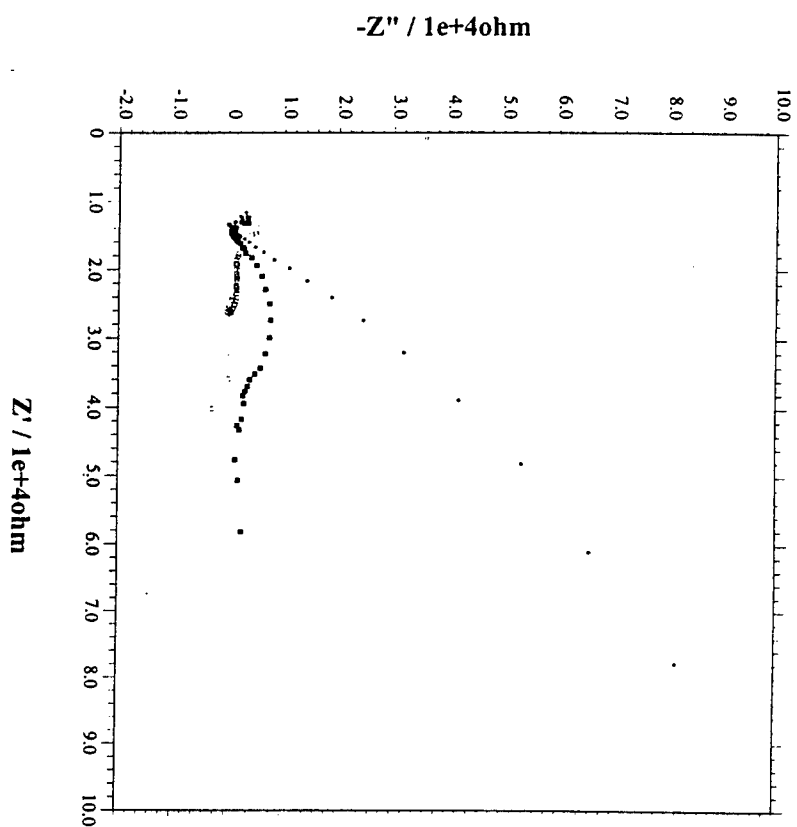
17

Fig. 17: Nyquist Plots of the PEG-Phenol Polymer Sol Gel Electrolyte under Bias: 0 V (∗), 1 V (■), 2 V (○)
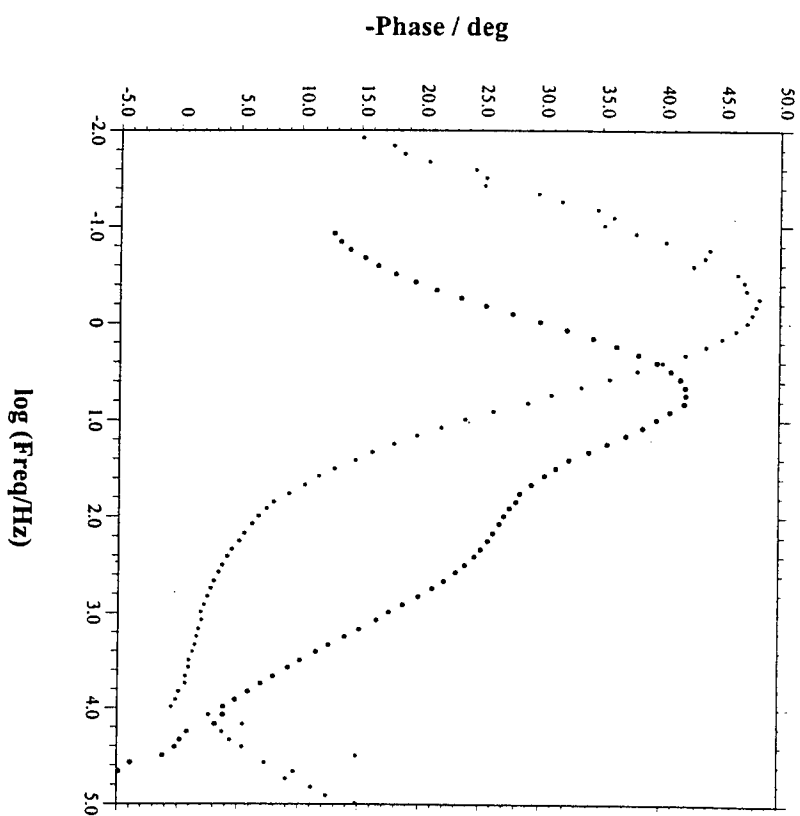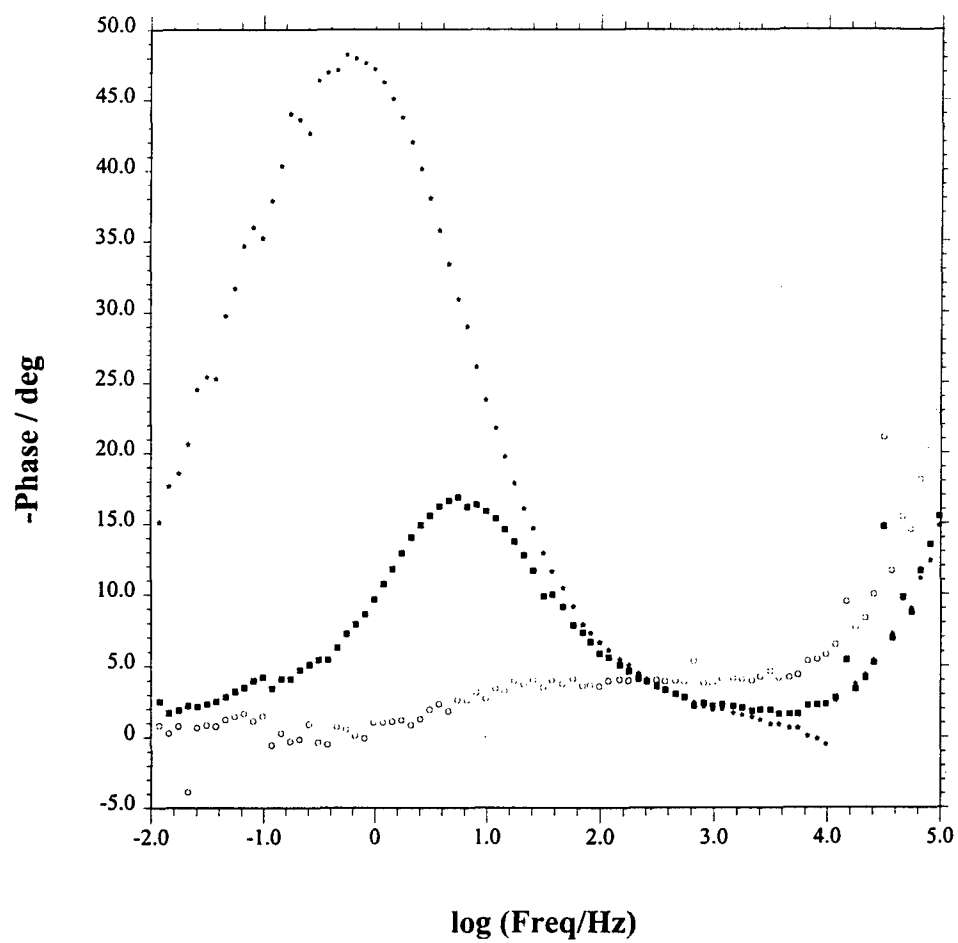

Fig. 18: Current-Voltage Phase Angle Shift of PEG-Phenol Polymer (●) and its Sol Gel Equivalent (∗)

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Fig. 19: Current-Voltage Phase Angle Shift of PEG-Phenol Polymer Sol Gel under Bias (Fig. 17 Data)

Current / 1e-5A

Time / sec

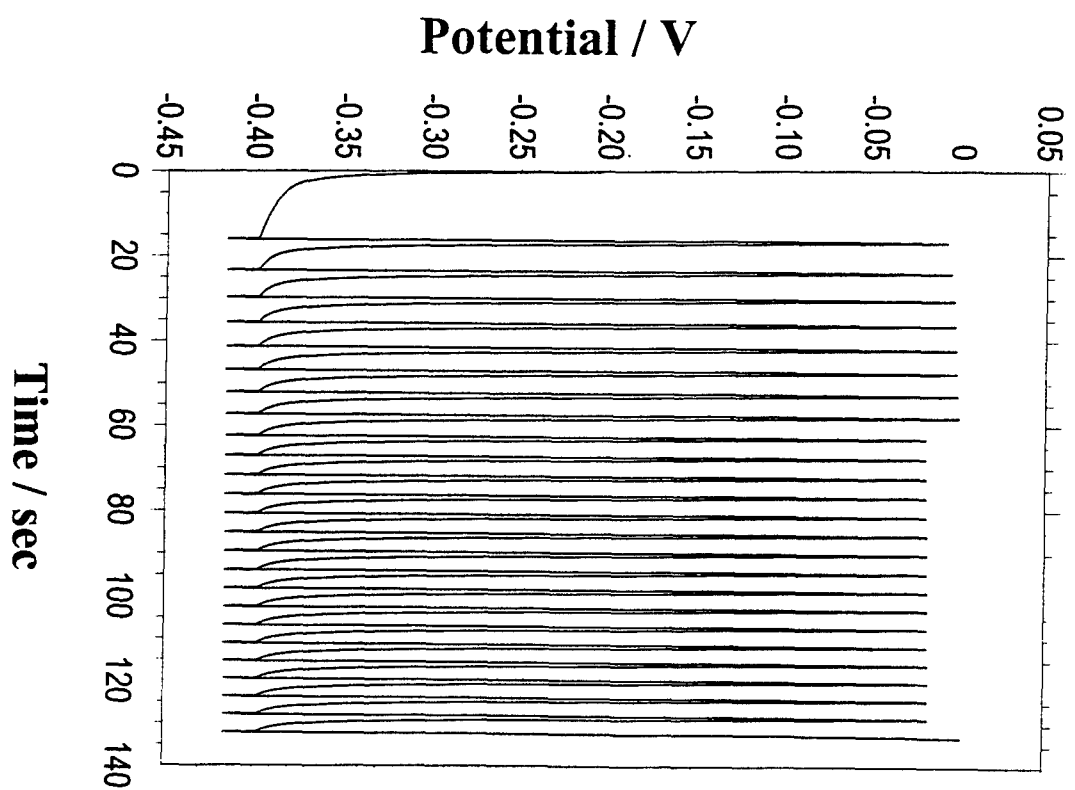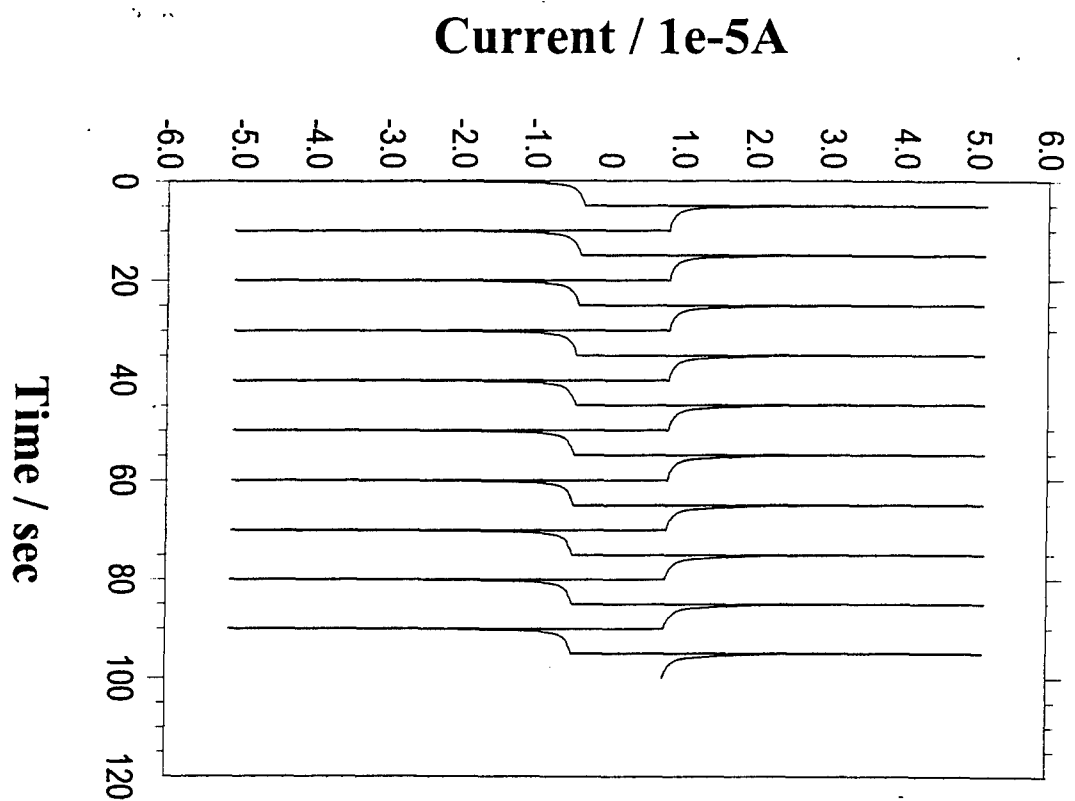**Potential / V**

Time / sec

Fig. 20: Cycling of the SS-TiN/Sol Gel Polymer Electrolyte/TiN-SS Cell using Chronoamperometry (*left*) and Chronopotentiometry

Furthermore, the magnitude of the current or voltage *vs.* time in both techniques remains the same regardless of the cycle number. This means that the electrolyte is stable during this cycling procedure.

Polymer Electrolytes based on Solvent-Free Gels: This is a preliminary evaluation of the gels prepared as described in the synthesis section. EIS analysis was carried out for the polymer gel as-synthesized without the incorporation of our PEG-phenol polymer, and with the lithium salt such that the molar ratio of Li/O is 1/8. The ionic conductivity determined from the Nyquist plots was determined to be approximately 10^{-6} S/cm for the polymer gel and 5×10^{-5} S/cm for the polymer gel/lithium salt. These numbers could be substantially improved once our polymer is incorporated within the gel during formation of the latter. This process will ensure that the PEG segments will be locked in the gel matrix and be allowed to interact with the six PEG repeat units of the gel proper. This effort would be investigated further in the Phase II program. These gels are flexibility and tough due to the network formed during gelation in the conditions we have used. Other advantages include, excellent wetability of the electrodes, absence of solvents (as is well-known in "polymer gel electrolytes") and ease of fabrication

Lithium Ion Battery:

According to impedance analysis and four-probe measurements, the highest bulk ionic conductivity of our polymer electrolyte was found to be 8×10^{-4} S/cm as mentioned above. This value was obtained with the experimental 3M *HQ117* salt, which is being used in the current 3M polymer batteries. With such a level of conductivity, a polymer electrolyte layer thickness can be anywhere from few μms to 1 mm. In general, an electrolyte layer with a conductivity of 10^{-6} S/cm, is considered good for lithium ion batteries, as long as it's thickness does not exceed few μms. Since our electrolyte has a conductivity of the order of 10^{-3} S/cm, and could still be improved, the layer thickness can be as thin as 1 μm and as thick as few millimeters. This is particularly interesting due to the fact that the material can easily be formed into thin films with good wetability.

The batteries were assembled using a carbon-filled elastomer (used by Evans Capacitor Co. in their electrochemical capacitors) as the conductive substrate and current collector. The polymer electrolyte was then deposited as a thin layer (approx. 100 μm) onto the cathode material, which consisted of $LiCoO_2$ in one case and $LiMnO_2$ in another case. Both are available from E-Tek Co., Natick, MA. The lithium anode (Aldrich) was placed onto the coated cathode. The anode/electrolyte/cathode assembly was sandwiched between two current collector sheets (Evans conductive elastomer) and heat-sealed at the non-conductive periphery provided by a sealant (**Fig. 21**). With such a construction, good contact is ensured between the different components. This assembly was carried out in a glove bag under nitrogen to avoid passivation of the electrodes during testing. The advantage of such an assembly is the possibility of manufacturing of different designs including stacking of various cells or the rolled-type battery due to the good flexibility of its various components. Battery testing was performed using chronopotentiometry and other electrochemical techniques.

Conductive Elastomer — *Li Anode*
Polymer Electrolyte
LiCoO₂ or LiMnO₂ Cathode — *Sealant*
Conductive Elastomer
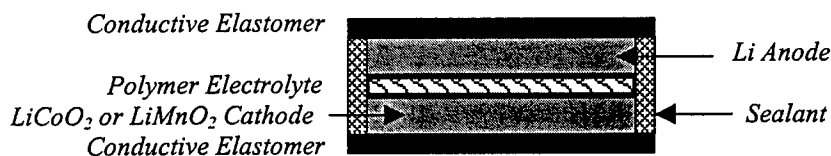
Fig. 21: Cross-sectional View of the Fractal Systems' Lithium Ion Polymer Battery

Room-Temperature (RT) Studies: Using $LiCoO_2$ as the cathode material, the flexible polymer battery had an open circuit voltage (V_{oc}) of 3.7 V *vs.* lithium (used as the anode and reference electrode). The

battery was charged and discharged at various current densities. We wanted to find out whether it could withstand cycling, first at room temperature, using high current densities, which would make it competitive with existing technology. **Fig. 22** shows two charge and discharge cycles, cycle # 1 and cycle # 30, at 200 μA/ cm^2. The battery was allowed to charge and discharge at all cycles for 120 seconds. *First*, It s important to note that very little difference is observed between the first and 30th cycles. This indicates stability of the battery and absence or minimal side reactions occurring between the electrolyte and the lithium metal, as is usually the case with most polymer electrolytes. *Second*, the coulombic efficiency calculated from the area under the charge and discharge curves for each cycle is approximately 95%. This is an excellent number for a solid-state polymer battery. *Third*, a 2-minute discharge ends with a voltage of 2.4 V at the first cycle and 1.7 V at the 30th cycle. Ending up with such voltages means that the battery has a good discharge capacity. *Fourth*, The charge and discharge curves, after the initial increase or decrease of the potential respectively, are flat. Therefore, we consider such cells as constant potential batteries, and this is typical of lithium ion batteries.

LiMnO$_2$ was used in the second type of battery as the cathode material. Here again, the coulombic efficiency was very good and comparable to that of the previous one. The discharge curves at room temperature for cycles # 3 and 4 are shown in **Fig. 23**. The V_{oc} of such cell is 3.45V *vs*. lithium. The discharge was conducted using a 50 μA/ cm^2 discharge rate for one hour. As can be seen from these plots, the voltage at the end of a long-term discharge is 2.65 V, a value which is quite good, and indicates that the battery could be discharged at such current density for much longer periods of time. Here again, the fact that the discharge curve stays flat after the initial decrease in potential is indicative of the cell's excellent characteristics during discharge, with the absence of side reactions. The LiMnO$_2$-based cell seems to offer a higher charge capacity and stability than the previous one.

Studies at Temperatures < RT: Although, this study is one of the focal points to be stressed in the Phase II program, we wanted to conduct an evaluation of our battery systems at temperatures lower than RT. Charge/discharge studies were conducted on the same cells used for the RT studies. **Fig. 24** shows these results, obtained using chronopotentiometry, for the LiCoO$_2$ system at 10°C up to 10 cycles. A discharge current of 50 μA/cm^2 was used for 30-min charge and 30-min discharge steps. As can be noticed from these rsults, there is very little polarization upon cycling. The potential decreases - 2.2 V *vs*. Li then stays flat for the remainder of the discharge period, which is the expected characteristic. The LiMnO$_2$ system was studied as well. In **Fig. 25**, we plotted the charge/discharge cycles at 50 μA/cm^2 for 30 min per step at 2°C. The potential becomes flat after few minutes and the final potential after 30 minutes is 1.9 V at the end of the 1st discharge. This potential is decreased to 1.3 V at the end of the 15th discharge. These polarization figures are promising considering the low temperature performance. The coulombic efficiency upon cycling is good here as well. It is important to note that the flat behavior of the discharge curves starts immediately at discharge. This means that the battery can be rated at the voltage given by the average value of the flat sequence of the curve. Also, the charge capacity is quite high, considering that discharge stays flat for longer periods of time.

Conclusions

Based on the various studies we have carried out in this Phase I program, we have demonstrated that polymer electrolytes can be prepared efficiently and at low cost using environmentally benign starting materials *via* non-conventional synthesis means, namely, through enzyme catalysis. A conductivity approaching 10^{-3} S/cm for a totally solid-state system (solvent-free) is unprecedented. It is considered as a viable number for justifying further development towards market potential. The use of the polymers, when combined with the appropriate lithium salt, as a stand-alone system, or in the form of a sol gel material, in lithium ion batteries has been successfully demonstrated between 0°C and RT. The following
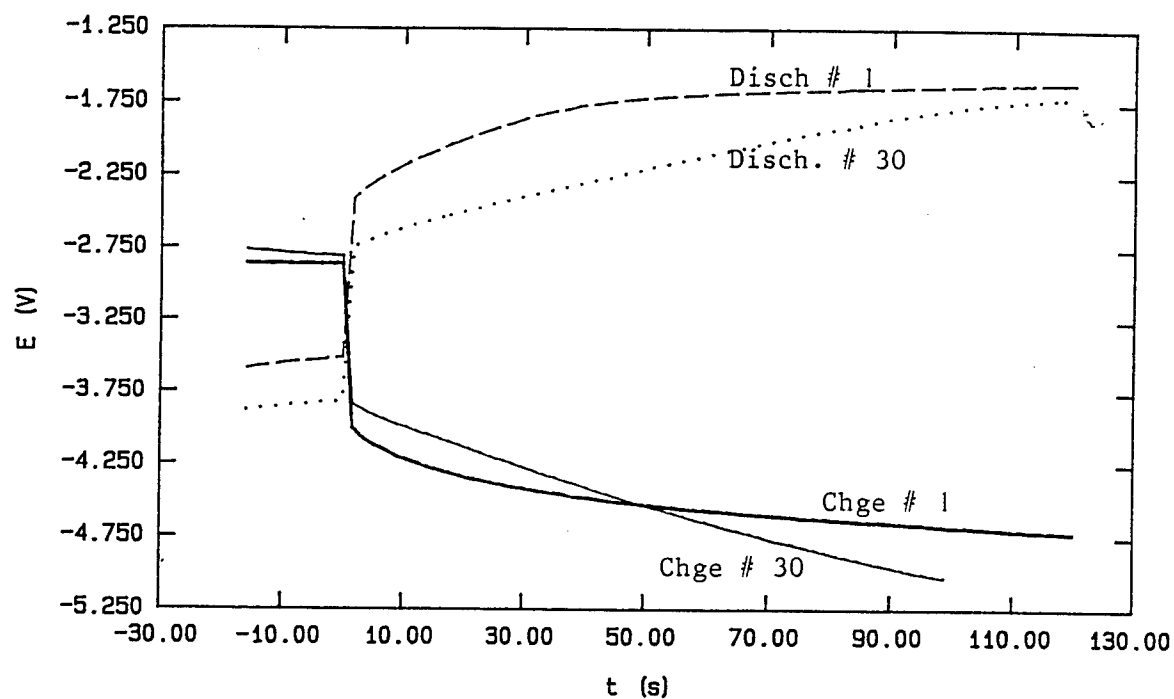
Fig. 22: Charge/Discharge Characteristics of Li/Polymer Electrolyte/LiCoO₂ Battery at 200 μA/cm²
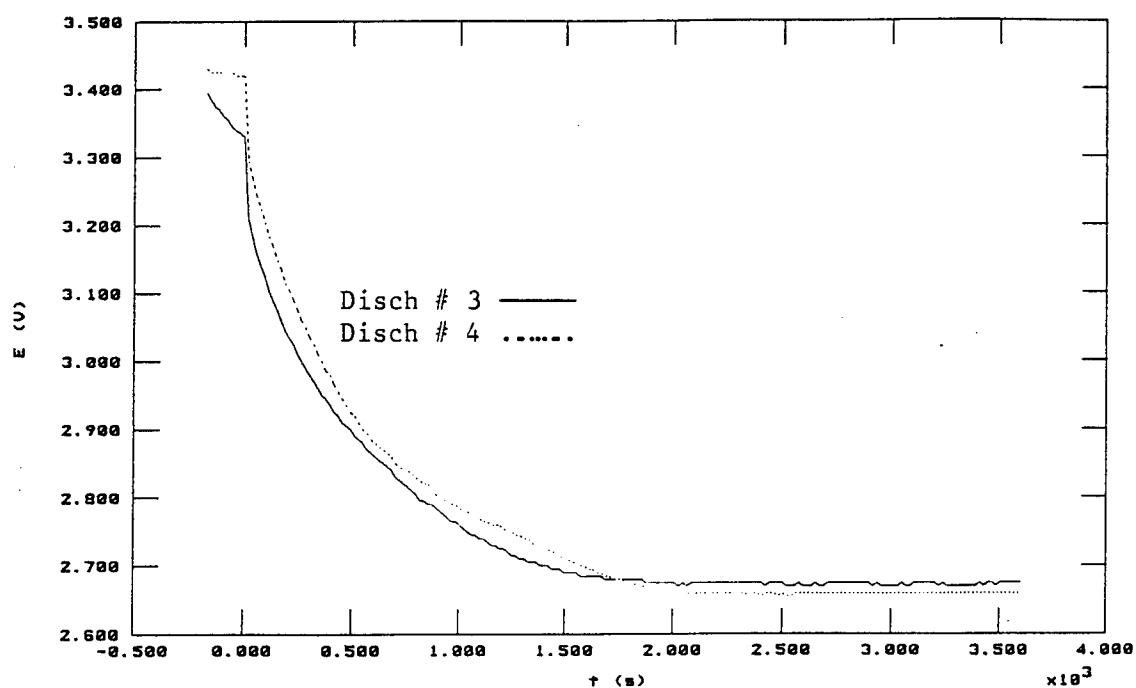

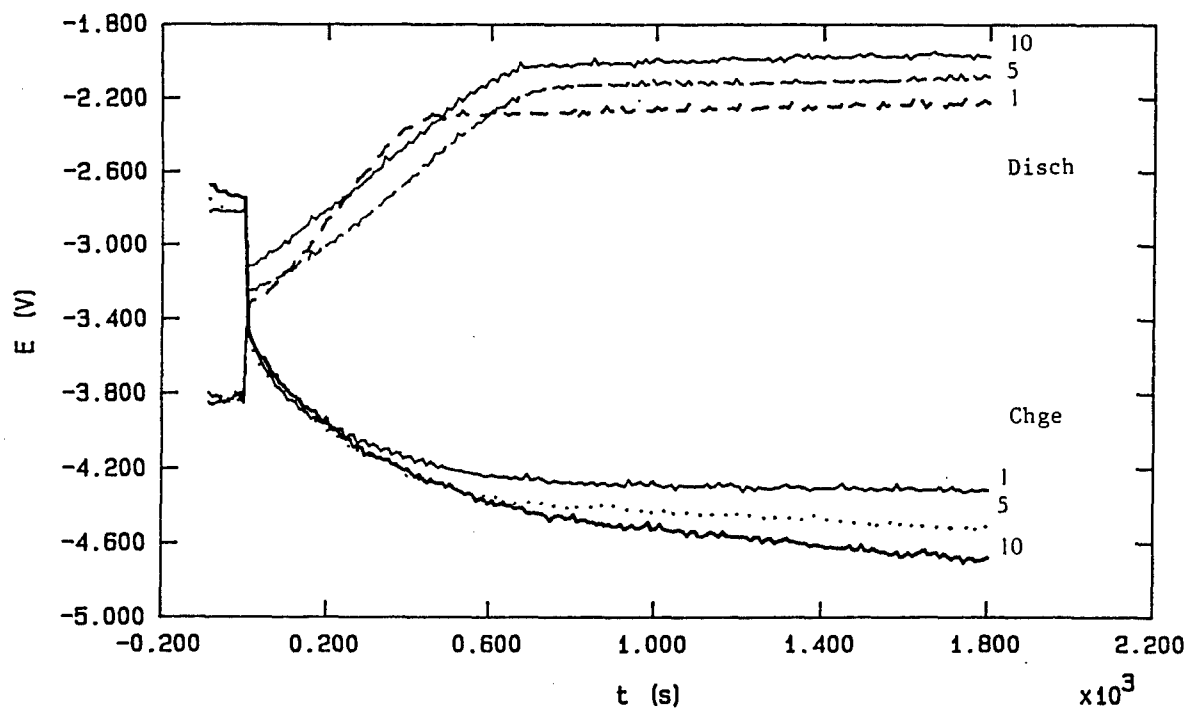**Fig. 23: Discharge Characteristics of Li/Polymer Electrolyte/LiMnO₂ Battery at 50 μA/cm²**

Fig. 24: Charge/Discharge of Li/Polymer Electrolyte/LiCoO₂ Battery at 50 μA/cm² and 10°C

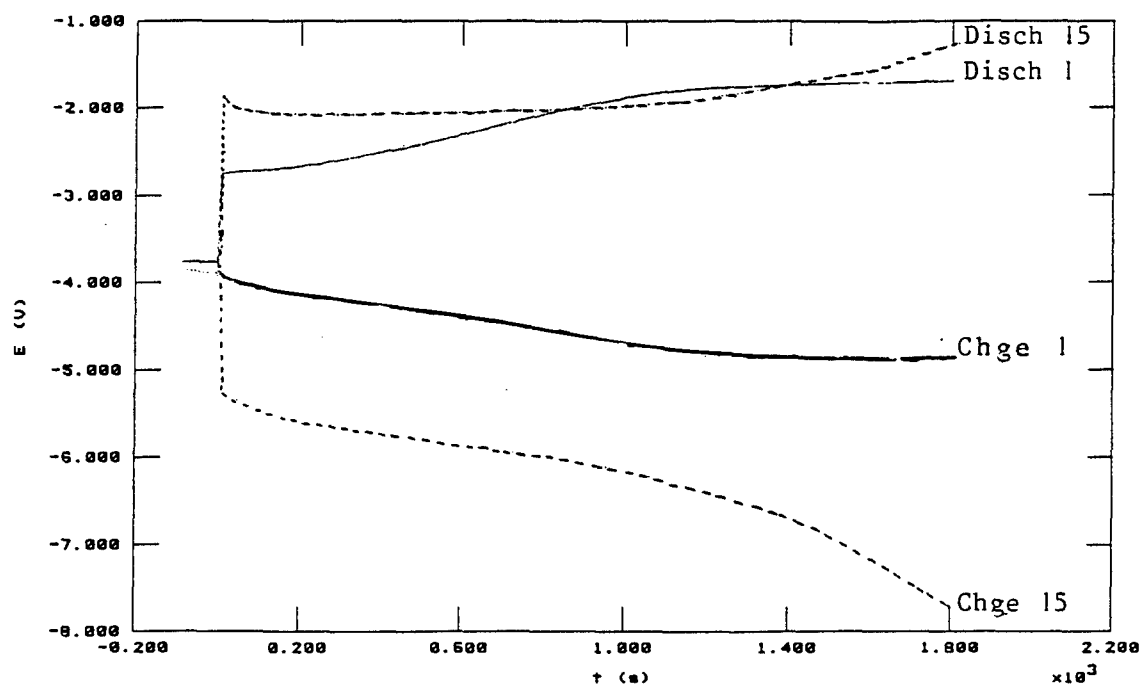**Fig. 25: Charge/Discharge of Li/Polymer Electrolyte/LiMnO₂ Battery at 50 μA/cm² and 2°C**

two sections summarize our plan for pursuing a full development program with a commercialization strategy that is likely to succeed in the short term following Phase II.

Phase II Program Outline

Because we have shown that enzyme catalysis can result in the synthesis of polymer electrolytes easily, and with low-cost environmentally benign starting materials, the scale up of the synthesis will be an easy and necessary task for the development of a high performance electrolyte system for lithium ion batteries. Based on our Phase I results, we will carry the following tasks in the Phase II program:

- Synthesis of the sulfonated polymer electrolyte and comparison with the non-sulfonated one;

- Polymer synthesis scale up and optimization of the process;

- Full characterization of the polymer in order to establish synthesis specifications;

- Preparation and optimization of the sol gel formulation based on our optimized polymer electrolyte;

- Use of our sol gel polymer electrolyte in a lithium ion battery for full electrochemical characterization in a range of -40°C to +70°C;

- Use of an improved version of the polymeric current collector by sputterring with a layer of carbon to improve contact resistance with the electrodes;

- Use of the state-of-the-art electrode materials as they become commercially available or sampled on an experimental basis, such as the tin sub-oxides; and

- Delivery of status reports, a final report and a prototype of a representative battery system based on our program by the end of the Phase II contract together with a commercialization report.

Commercialization Strategy

We have already started this effort in collaboration with Evans capacitor Co., who supplies the current collectors, and who will supply the improved ones for Phase II. The assembly of the batteries will take place at Fractal Systems Inc. using our solvent-free electrolyte, commercially available anodes and cathodes, and Evans' current collectors and sealing material. First, customers of Evans' Capattery® will be targeted with our products, and specifications, based on needs, will be determined prior to building few prototypes towards the end of the Phase II program. The marketing effort together with Evans will commence in the third quarter of the program, and will be extended to other customers as we progress in this effort.

References

1. F. Croce, F. Gerace, G. Dautzenberg, S. Passerini, G. B. Appetecchi and B. Scrosati, *Electrochim Acta* **39**, 2187 (1994).

2. L. H. Sperling, *Introduction to Physical Polymer Science,* 2nd ed., p. 429, John Wiley & Sons, Inc., New York (1993).

3. J. A. Akkara, K. Senecal and D. L. Kaplan, J. Polym. Sci., Polym. Chem. **29** (1991) 1561.

4. M. S. Ayyagari, K. A. Marx, S. K. Tripathy, J. A. Akkara and D. L. Kaplan, Macromol. **28** (1995) 5192.

5. O. Hankovszki *et a.l, Journal of Medicinal Chemistry* **29**, 1138-1152 (1986), Table II, Compound 4C.

6. K Yamashita *et al., JACS* **117**, 6249 (1995).